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RESEARCH MEMORANDUM

SPONTANEOUS IGNITION LIMITS OF PENTABORANE

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SUMMARY

An investigation of the spontaneous ignition limits of pentaborane-air mixtures was made at 25° C and pressures ranging from 0.3 to 76 centimeters. The lean limit of spontaneous ignition determined in 6-centimeter-diameter spherical bulbs was approximately 14 volume percent at 1 atmosphere and about 55 volume percent at 0.1 atmosphere. The rich limit was not determined, but mixtures containing 75-percent pentaborane ignited at 5 centimeters of mercury. Stable mixtures of pentaborane and air could not be obtained by addition of air to pentaborane vapor at 25° C except at pentaborane pressures less than 0.2 centimeter. Pentaborane-air mixtures that are outside the flammability limit may be prepared by slowly evaporating pentaborane into air or, under some conditions, by spraying pentaborane into air. When air was introduced on or below the surface of liquid pentaborane at 25° C or less, any explosions that occurred were in the vapor-air mixture above the liquid.

INTRODUCTION

Current interest in the use of pentaborane (B_5H_9) and pentaborane-hydrocarbon blends as aircraft fuels has resulted in an increasing need for information about the spontaneous flammability of these fuels. Available information on the subject is somewhat contradictory. Price (ref. 1) reports that pentaborane-air mixtures are spontaneously flammable over a very wide range of compositions, while Stock (ref. 2) states that pentaborane is not spontaneously flammable. The authors of reference 3 observe that pentaborane ignites spontaneously only under certain conditions.

Fletcher (ref. 4) also reported on the conditions under which pentaborane inflamed and those under which it could be safely handled in experimental work. It was suggested by reference 4 that spontaneous ignition would probably result only when liquid pentaborane was present. The present study was undertaken to investigate further the spontaneous flammability of liquid and vapor pentaborane. The findings should contribute to safety in handling pentaborane.

The reaction between liquid pentaborane and air was investigated at room temperature and below by bubbling air through the liquid. These studies suggested that an investigation be made of the vapor-phase reactions. Spontaneous ignition limit studies were conducted over the range of concentrations permitted by the saturation vapor pressure of pentaborane at room temperature in 6-centimeter-diameter spherical bulbs at pressures of 1 atmosphere and below. Previous experimental data are discussed in the light of these new data. A consistent picture of the spontaneous ignition of pentaborane-air mixtures results.

PROCEDURE AND RESULTS

Liquid-Phase Studies

The vacuum line used for the storage and transfer of pentaborane is shown in figure 1. The units shown in figures 2(a) and (b) were used to study the reactions between liquid pentaborane and air. After the glass apparatus (fig. 2(a)) was evacuated, pentaborane was condensed into the bottom of the tube by applying a -80° C bath. Air was admitted to the liquid pentaborane through a tube sealed into the side of the vial. A thermocouple connected to a recording potentiometer recorded the temperature changes in the liquid. The surface of the liquid was above the air inlet tube in some experiments and level with it in others. The only material initially present above the liquid in the vial in figure 2(a) was pentaborane vapor.

The tube in figure 2(b) was also evacuated by connecting it to the vacuum line and partially filled with pentaborane by applying a -80° C bath to the sealed end. In this experiment, however, air or nitrogen was added to the space above the pentaborane. The tube was then removed from the line and positioned under a thermocouple and an air supply tube as indicated in the figure.

The following results were obtained in all experiments when air was admitted to liquid pentaborane at 25° C or below:

(1) A reaction, indicated by a flash and audible sound, occurred in the gas phase some distance above the liquid.

(2) No increase in temperature in the liquid was observed until after this reaction above the liquid, and then the increase was approximately 5° to 10° C.

(3) No visible reaction was ever observed in the liquid.

The following observations were also made:

(1) The thermocouple indicated a decrease in temperature just prior to the reaction in the gas phase when placed at the surface of the liquid rather than below. This decrease probably resulted from the evaporation of pentaborane.

(2) Although the reaction was never violent enough to break the vial (fig. 2(a)), it did blow out the stopcock on the air inlet tube.

(3) The reaction occurred almost instantaneously with the admission of room-temperature air when air was initially present above cool pentaborane, and was slowest in occurring when N_2 was initially present.

(4) In experiments with air or N_2 initially present above the cooled liquid, a blue flame appeared at the mouth of the tube after the first explosion and continued to burn there until all the liquid had evaporated. In some cases the blue flame was disturbed by several flashes of yellow flame, which shot upward above the mouth of the tube.

Vapor-Phase Studies

Spontaneous ignition limits were determined in 100-milliliter spherical glass bulbs (6-cm diam.) which were equipped with a stopcock and standard joints as shown in figure 2(c). The vacuum line in figure 1 was again used for the storage and transfer of pentaborane. A given amount of pentaborane vapor was condensed in the bulb at -80° C, and a given quantity of air added. The bulb was detached from the line and allowed to warm up to room temperature (25° C). If a reaction occurred, a flame appeared in the bulb and a brown deposit covered the walls. On some occasions the reaction was so violent that the unit was broken.

In figure 3 the results of this study are plotted in terms of the partial pressure of air present in the mixture and the partial pressure of pentaborane that would result on complete evaporation of the liquid. The circles in the plot indicate mixtures formed by the preceding technique which did not ignite; the squares represent compositions which presumably could not be obtained since spontaneous ignition took place during their formation. A solid curve was drawn between these points to separate the region of ignition and nonignition. A dashed line based on the results of reference 3 indicates the rich limit. The region to the left of the solid curve and below the dashed curve indicates the composition of pentaborane-air mixtures that are stable at 25° C; mixtures having compositions in the region bounded by the two curves will spontaneously ignite under the conditions of the test. An alternative method of presenting the results is shown in figure 4, where the total

pressure is plotted against the volume percent of pentaborane. Pressures of pentaborane are given only to 20 centimeters in figure 3, since this is the saturation vapor pressure of pentaborane at 25° C. The region not permitted by this vapor-pressure limit is also shown in figure 4. A vapor-pressure curve from reference 5 is given in figure 5.

As shown in figure 3, only mixtures containing a partial pressure of less than 0.2 centimeter of pentaborane were stable at all pressures below 1 atmosphere. A few experiments were conducted at 0° C. At this temperature pentaborane-air mixtures containing partial pressure of <3.0 centimeters of pentaborane were stable at all pressures below 1 atmosphere.

DISCUSSION

It is suggested that, under the conditions of the experiments reported herein, liquid pentaborane is less reactive than the vapor in contact with air at 25° C and below. This observation is based on the fact that ignition and burning always took place well above the liquid and that the temperature of the liquid remained fairly constant and very close to room temperature. The slight increase in temperature (5° to 10° C) probably resulted from the heat conducted from the gas-phase reaction. If the liquid had been the source and center of the reaction, the temperature therein should have increased appreciably. An examination of photographs of an experiment in which a 10-cubic-centimeter sample of liquid pentaborane was sprayed into a test tube (ref. 4) also showed that the source of ignition was not in or on the surface of the liquid but some distance above. Since liquid pentaborane serves as a source of vapor, which appears to ignite spontaneously at the proper pressure, it is obviously a potential hazard.

It will be seen that all previously reported observations on the spontaneous ignition of pentaborane can be explained on the basis of the ignition limit curve. The previous observations on the ignition of pentaborane and air can be divided into two general classes:

A. Addition of air to pentaborane vapor

(1) A flash resulted when air was rapidly admitted to pentaborane vapor. (No further data given (ref. 3).)

(2) Ignition occurred when air was rapidly admitted to a 250-milliliter bulb containing 2.9 centimeters of pentaborane vapor at room temperature (ref. 4).

(3) Ignition occurred when air was allowed to rush into a tube containing liquid pentaborane (with only pentaborane vapor above it) at room temperature (ref. 4).

(4) Adding air to relatively low pressures of pentaborane (about 1.0 cm) produced spontaneous ignition as did the addition of air to high pressures (about 20 cm) (ref. 6).

(5) In a 4.2-centimeter-diameter bulb spontaneous ignition did not result upon addition of air, if the pentaborane pressure was below 0.25 centimeter (ref. 6).

Observation (1) may be explained by starting with a given pressure of pentaborane vapor, such as 5 centimeters (point A on fig. 3), and adding a quantity of air. If 4 centimeters of air is added, a spontaneously flammable mixture will be formed (moving from point A to B in fig. 3). If a larger amount of air had been admitted so as to reach composition C, ignition would also have occurred. While the mixture C is stable, the method of preparing it involved going through a region of spontaneous flammability. At some instant in the preparation of this mixture, compositions and pressures existed which were within the flammable zone and thus ignition resulted. If stable mixtures of pentaborane and air are to be formed, a spontaneously flammable region obviously must not be crossed.

Observations (2), (3), and (4) on ignition resulting from the addition of air to pentaborane vapor are also explained by these findings. If this technique was used to determine the flammability curve, all mixtures of air and pentaborane, above approximately 0.2 centimeter pressure of pentaborane, would appear to be spontaneously flammable (observations (4) and (5)).

B. Addition of pentaborane to air

The mixing of pentaborane with air can occur by spraying liquid pentaborane into air or by evaporating pentaborane into air.

(1) No ignition resulted when sufficient pentaborane to form a stoichiometric mixture was quickly sprayed into air in a 241-cubic-centimeter bulb (ref. 4).

(2) Tubes containing 0.03 to 0.05 cubic centimeter of liquid pentaborane under nitrogen pressure were broken, discharging the pentaborane into air at 25° C; no reaction occurred (ref. 4).

(3) When these tubes were broken with a heated rod or in an air bath at 47° C, ignition resulted (ref. 4).

(4) A 10-cubic-centimeter sample ignited when sprayed into a test tube or evaporating dish at 27° C (ref. 4).

(5) No reaction was observed in experiments in which air was admitted to a vessel containing frozen pentaborane, which was then allowed to evaporate and become mixed with air by very slow warming to room temperature (ref. 3).

(6) If, in the preceding experiments, pentaborane was allowed to evaporate rapidly into air, flashing usually resulted (ref. 3).

(7) No ignition resulted when sufficient pentaborane to form a stoichiometric mixture was allowed to evaporate into a closed 200-cubic-centimeter bulb containing air (ref. 4).

(8) Ignition did occur in the preceding experiment when warm water was sprayed against the bulb during the evaporation period (ref. 4).

In experiments where pentaborane is sprayed into air (observations (1) to (4)), one moves along the line E-F (fig. 3), which represents a total pressure of 1 atmosphere. It is shown in figure 3 that, under the conditions used in this investigation, spontaneous ignition will not occur upon discharge of pentaborane into air unless the vapor pressure obtained is greater than 10 centimeters or, as shown in figure 4, unless the local concentration exceeds 15 percent. Observation (1) is consistent with these findings. In observation (2), a reaction probably did not occur because the quantity was too small to produce a local partial pressure of >10 centimeters. The higher temperature (observation (3)) may have increased the rate of evaporation and thus the concentration of vapor present in a local increment of volume, resulting in an explosive mixture. If a larger amount of the liquid had been present initially, a reaction should have occurred at room temperature. This is borne out by observation (4).

During the evaporation of a single drop, a rich concentration of vapor in the immediate vicinity of the drop might be expected. In the steady state, the exact concentration will be determined by the equilibrium or wet-bulb temperature of the drop. Estimation of wet-bulb temperatures for pentaborane suggests that, at room temperature, the wet-bulb temperature is too low to produce the vapor pressure necessary for ignition. (Indeed, air temperatures in excess of 60° C would be required.) The rate at which a droplet achieves the wet-bulb temperature is most rapid for small droplets (ref. 7). Accordingly, it seems reasonable that when pentaborane is dispersed into air as a fine spray, spontaneously flammable mixtures are not produced. Presumably with coarser atomization, or in the case of large liquid spills, the wet-bulb temperature is not obtained until after spontaneously flammable vapor-air mixtures are formed.

In observation (5) the path of preparation never crossed the ignition limit curve. If, for example, 5 centimeters of pentaborane were

frozen out and 25 centimeters of air added (point D on fig. 3), the resulting mixture upon warming to room temperature would be composition C. A similar explanation accounts for observation (7).

It is proposed that, in observations (6) and (8), a very high concentration of vapor was created in some incremental volume of the bulb by this rapid heating, thus entering the flammable side of the curve. For example, if only one-tenth of the total amount of pentaborane present in observation (8) had been suddenly heated to 30° C, the concentration of pentaborane in a volume of 5.5 milliliters or less would have given the conditions necessary for ignition. When mixtures are prepared by this technique, pentaborane should be allowed to evaporate slowly and, if possible, the temperature kept as low as will permit complete evaporation.

Two additional observations which combine both the addition of air to pentaborane vapor and evaporation of pentaborane into air are reported in reference 3:

(1) No ignition resulted when a vial containing about 2 grams of pentaborane was broken and its contents spilled on a laboratory bench. (No temperature given.)

(2) After a mixture of pentaborane and air was prepared by slowly evaporating frozen pentaborane into air, the pentaborane was recondensed, the air pumped off, and the pentaborane warmed to room temperature. Addition of air to this pentaborane again produced ignition.

The first observation may be explained if it is assumed that the initial pentaborane temperature was -10° C or less. No reaction would have resulted from air coming into contact with pentaborane vapor in the bulb at this temperature. If the spilled liquid formed a fairly shallow pool and evaporated very slowly, this quantity of pentaborane could probably evaporate without reacting.

The second observation is consistent with the results in figure 3. The path followed was from D to C, C to D, D to 0, and 0 to A. Ignition resulted when moving from A back to C.

Reference 4 showed that blending 3-methylpentane with pentaborane increased the temperature for spontaneous ignition. Blending hydrocarbons or JP-4 fuels with pentaborane to prevent spontaneous ignition would probably be effective if the quantity of fuel added reduced the vapor pressure of pentaborane below the ignition limit. Assuming that Raoult's law holds, the mole fraction of pentaborane at 25° C must be less than 0.7 to reduce the vapor pressure of pentaborane below the ignition limit under the conditions of this investigation.

In addition to limiting the pressure of pentaborane vapor by using blends, the pressure is automatically limited by the temperature as shown by the vapor-pressure curve (fig. 5). Spontaneous ignition did not occur upon evaporation of pentaborane into air at 1 atmosphere total pressure until the vapor pressure of pentaborane exceeded 10 centimeters (fig. 3). The vapor-pressure curve shows that a temperature of 10° C (50° F) is needed to obtain this pressure. Consequently, when pentaborane is evaporated into 1 atmosphere of air under the conditions of this study, spontaneous ignition should not occur at temperatures below 10° C.

The preceding discussion has tried to show that previously reported experimental findings are consistent with the results of this study. Although it was reported in reference 1 that gaseous pentaborane-air mixtures are spontaneously flammable, and in references 2 and 4 that they probably are not, the results of this work suggest that approximately half the composition region available at room temperature is stable. The apparent contradictions seemed to be resolved by examining the method of mixing. Stable mixtures of pentaborane and air may be prepared only by the proper paths and procedures.

The suggestion that liquid pentaborane must be present to obtain spontaneous ignition (ref. 4) does not seem to apply here, since the addition of air to almost all obtainable pressures of pentaborane vapor can cause spontaneous ignition. At high total pressure (proceeding along line E-F), ignition would definitely be expected if the concentration of pentaborane was high enough to produce liquid condensation. The results indicate that vapor concentrations below this value are probably spontaneously flammable, but the technique of preparing such mixtures involved the presence of liquid.

It must be strongly emphasized that the values reported herein are based on reactions in spherical 6-centimeter-diameter bulbs. While the results in this investigation can be used as a general guide in other situations, the exact values reported will apply only to the geometry used herein.

SUMMARY OF RESULTS

1. When air was introduced on or below the surface of liquid pentaborane at 25° C or less, any explosions that occurred were in the vapor-air mixture above the liquid.

2. The lean limit for spontaneous ignition of pentaborane vapor-air mixtures at 25° C determined in 6-centimeter-diameter bulbs was about 14 volume percent at 1 atmosphere, and about 55 volume percent at 0.1 atmosphere.

3. No rich limits of spontaneous ignition were determined; mixtures containing 75-percent pentaborane ignited at 5 centimeters of mercury pressure.

4. Except for very low pressures of pentaborane (<0.2 cm), the addition of air into pentaborane vapor caused spontaneous ignition at 25° C.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, February 7, 1955

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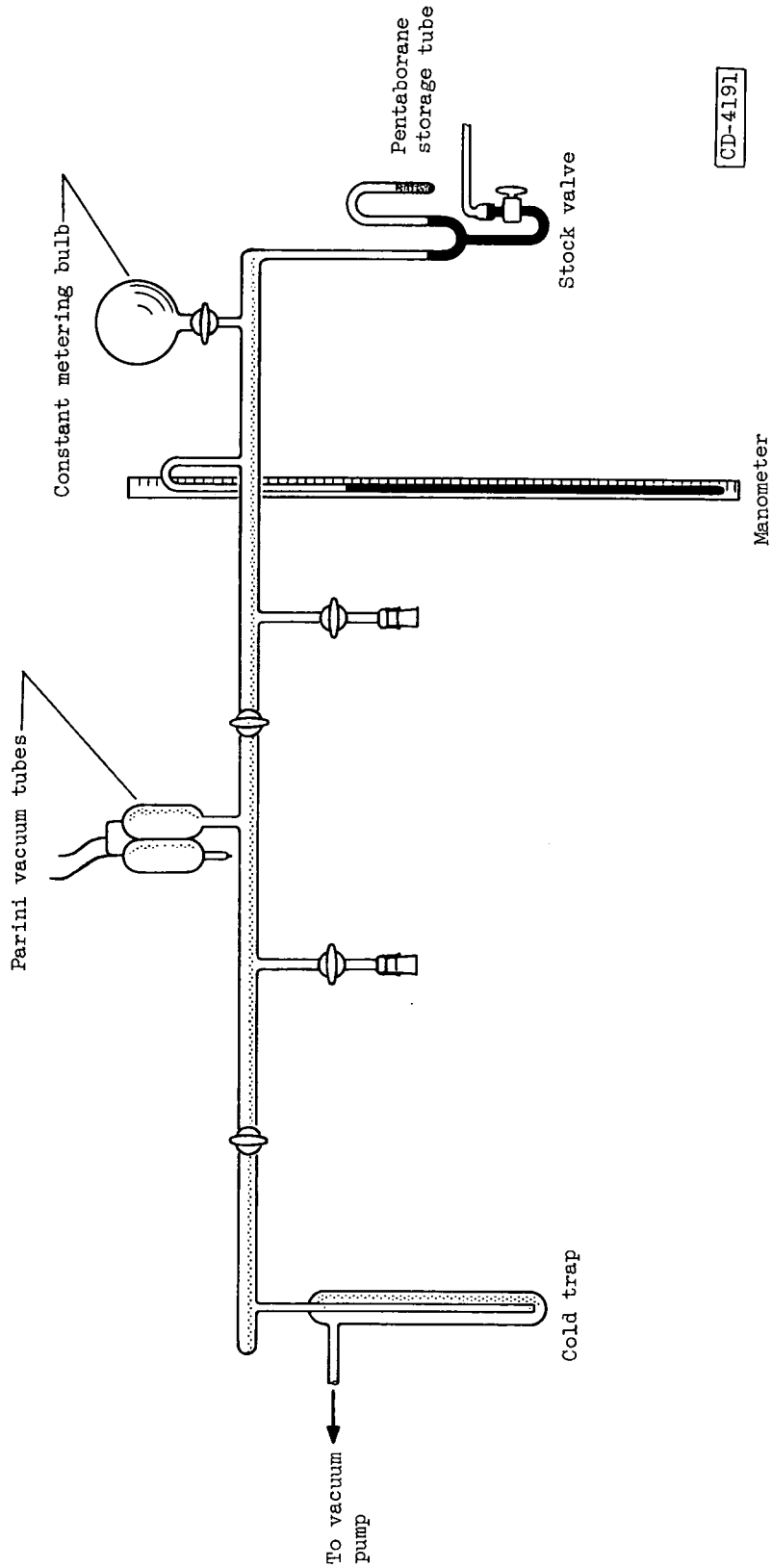
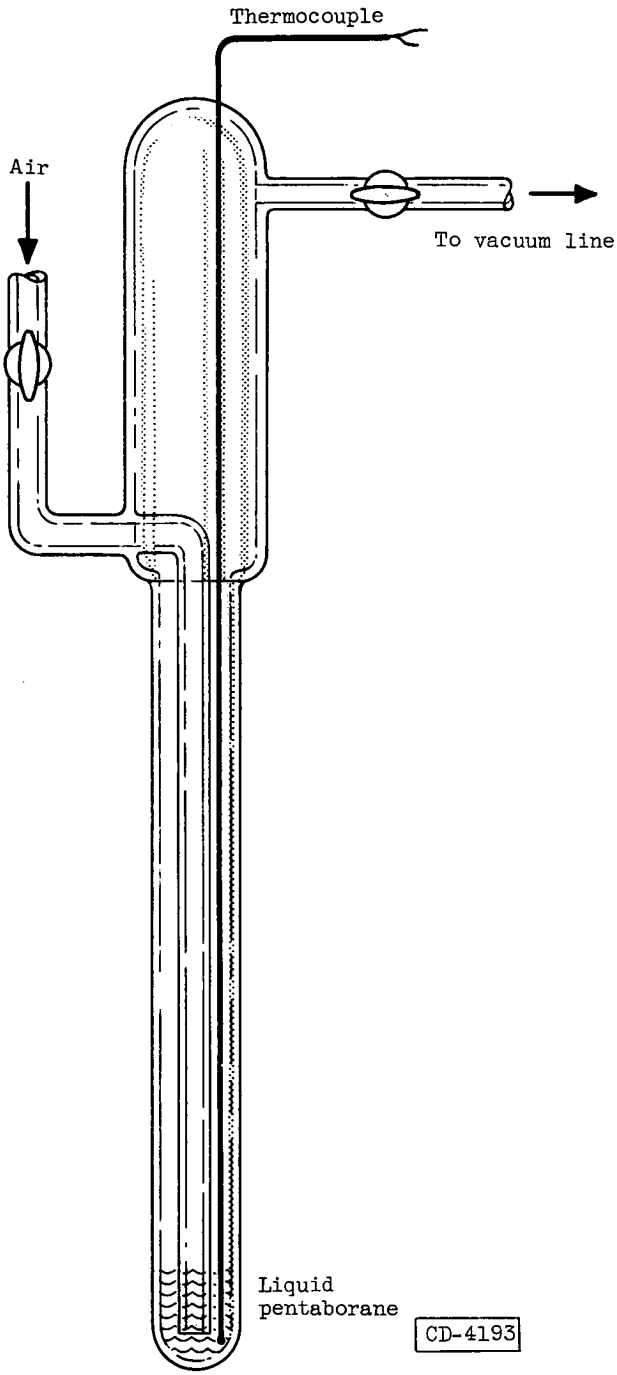
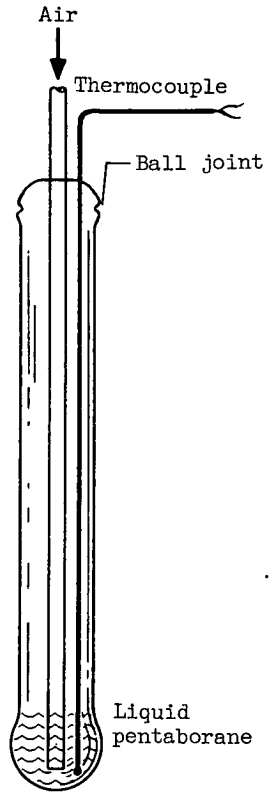


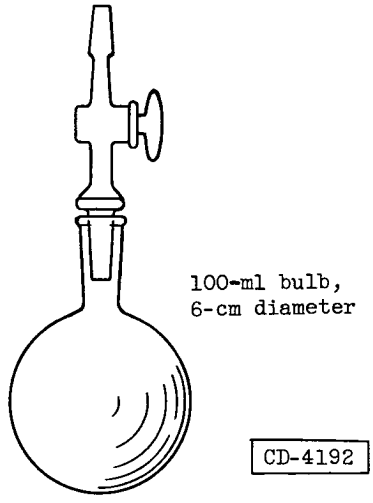
Figure 1. - Vacuum line for storage and transfer of pentaborane.



(a) Vial; liquid pentaborane and air.



(b) Tube; liquid pentaborane and air.



(c) Bulb; pentaborane vapor and air.

Figure 2. - Apparatus for studying reactions of pentaborane and air.

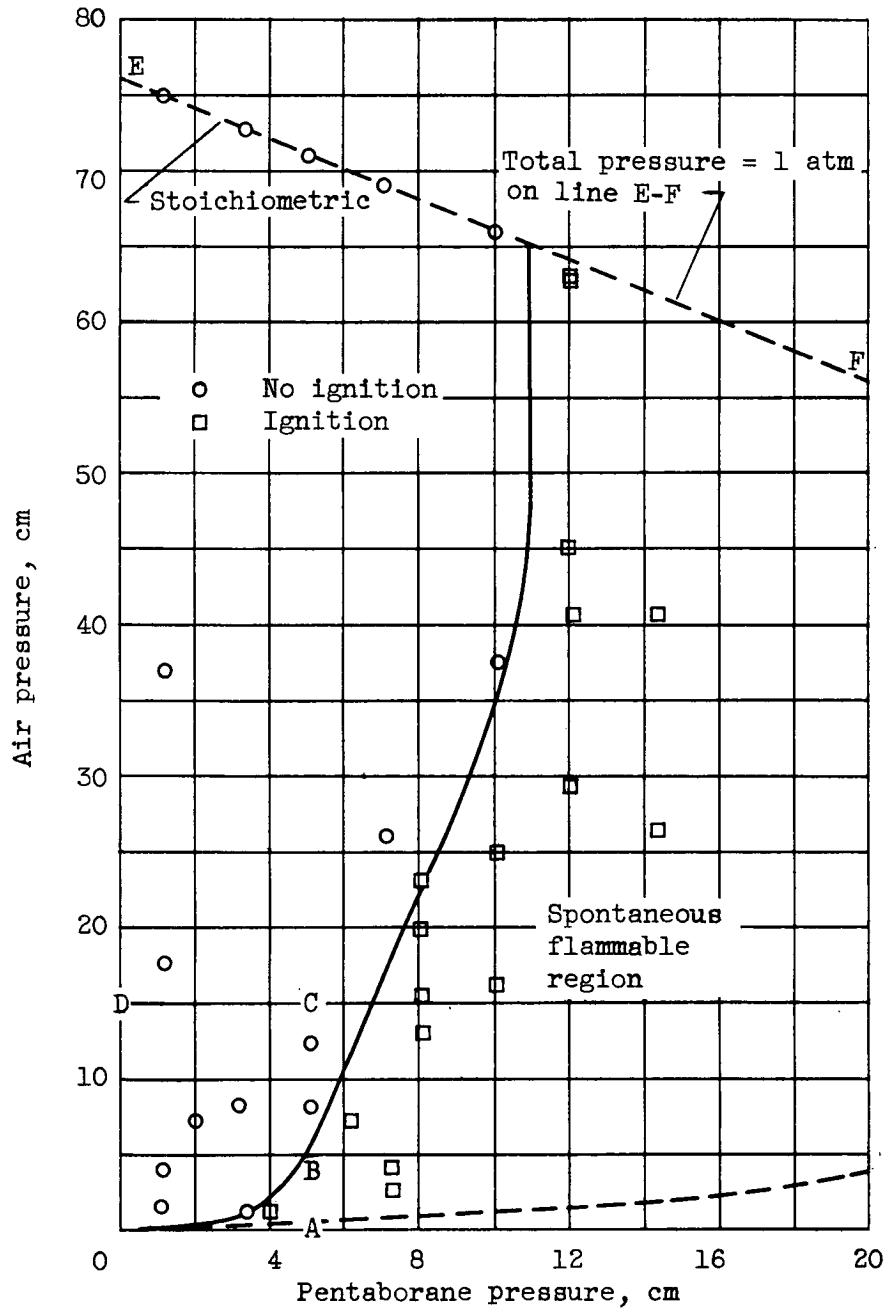


Figure 3. - Spontaneous-ignition-limit curve for pentaborane-air mixtures. Temperature, 25° C.

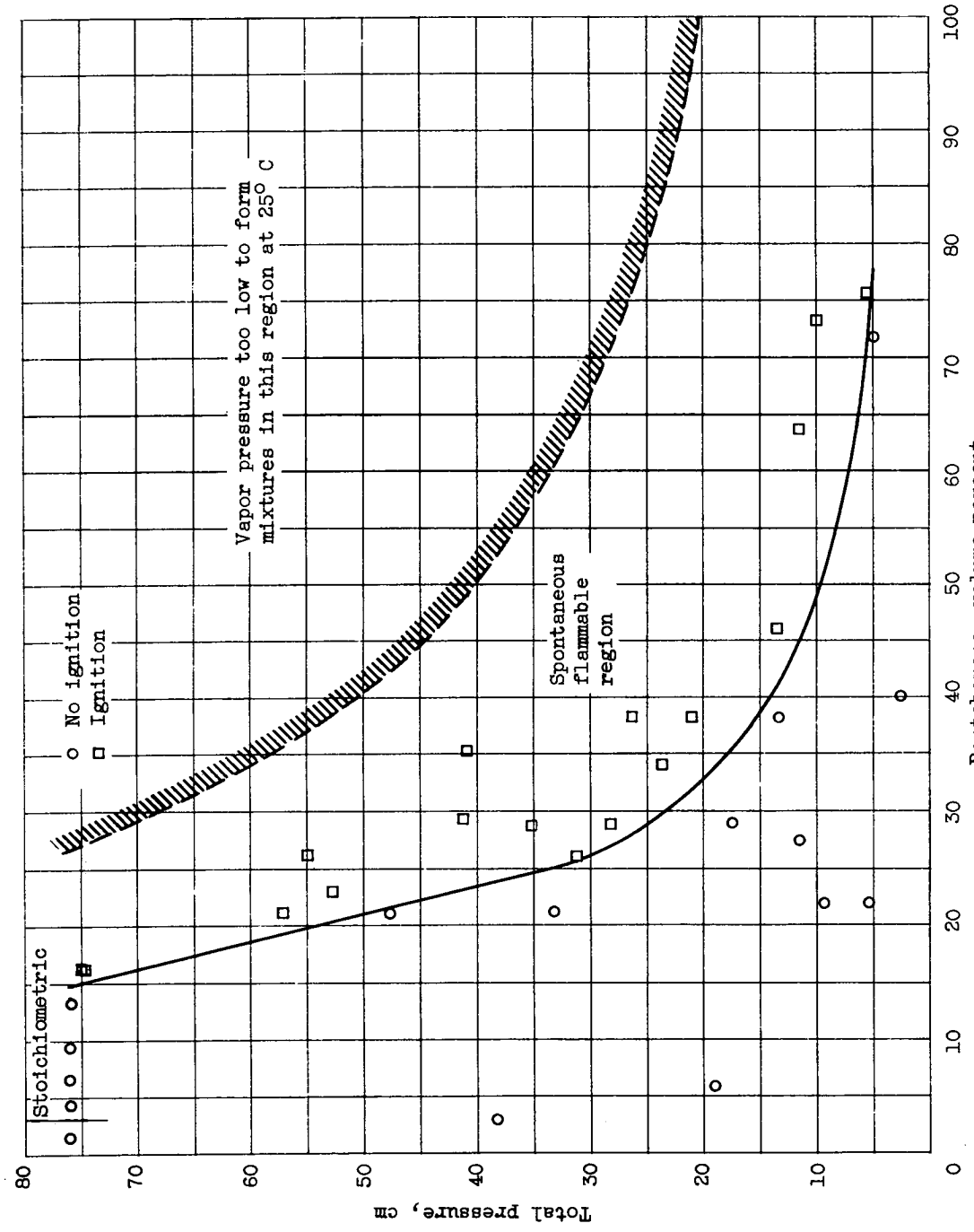


Figure 4. - Spontaneous-ignition-limit curve for pentaborane-air mixtures. Temperature, 25° C.

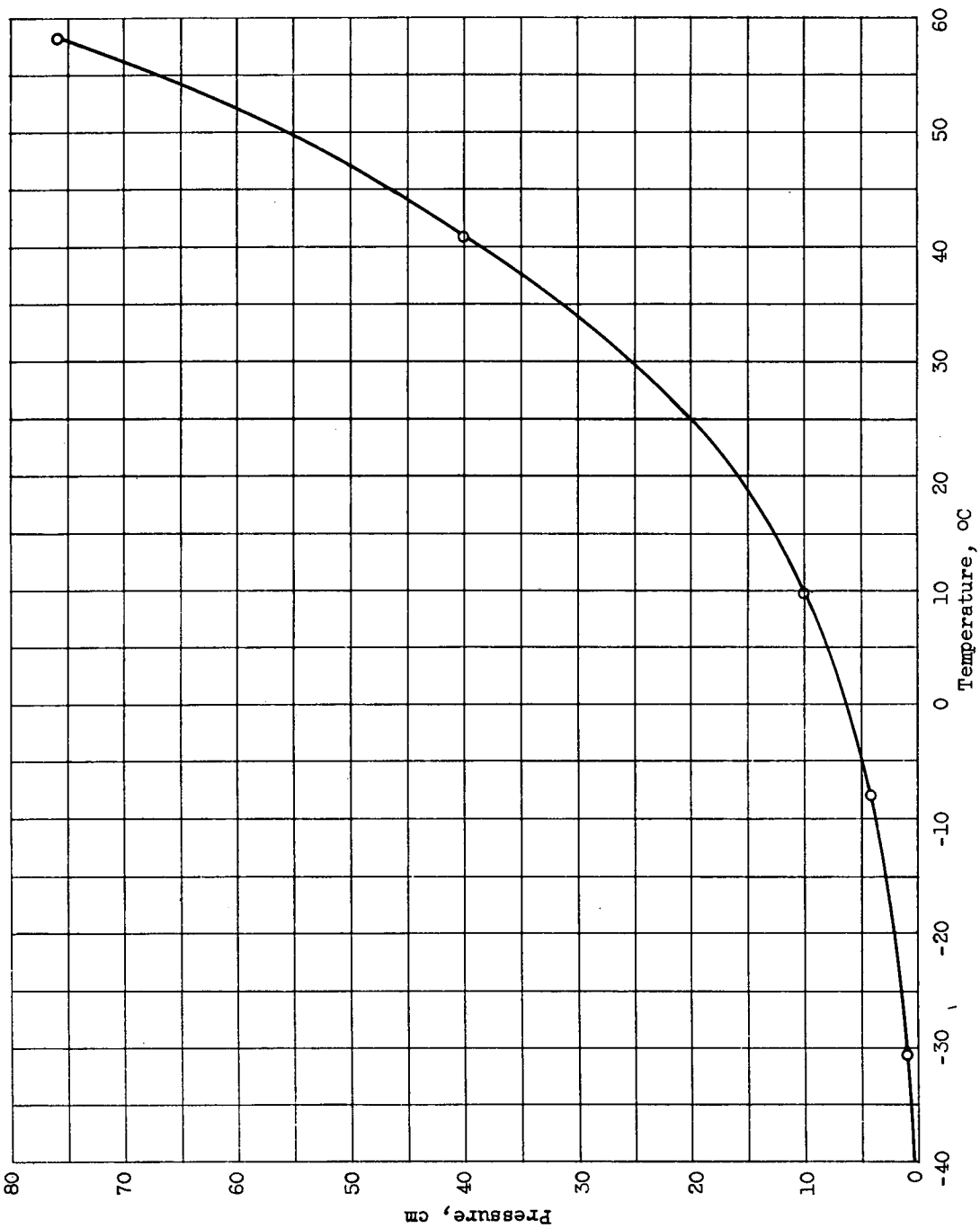


Figure 5. - Vapor pressure of pentaborane (ref. 5).